

Thermodynamics of Metal Complex Formation in Aqueous Solution. VIII. A Calorimetric Study of the Mercury(II) Thiocyanate, Selenocyanate, and Thiosulfate Systems

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The enthalpy changes for the formation of $\text{Hg}(\text{SCN})_4^{2-}$, $\text{Hg}(\text{SeCN})_4^{2-}$, and $\text{Hg}(\text{S}_2\text{O}_3)_3^{4-}$ have been determined calorimetrically by measuring the heats of solution of HgO in solutions of perchloric acid, thiocyanate, selenocyanate, and thiosulfate. From the enthalpy changes measured, and the free energy changes computed from the stability constants, the entropy changes have been calculated. All data refer to 25.0 °C.

The enthalpy changes for the three reactions studied are all highly exothermic. The entropy terms are rather small. For the thiosulfate system the entropy term is positive while those of the thiocyanate and selenocyanate systems are negative and consequently counteracting the complex formation.

In order to compare the coordinating properties of the analogous ligands thiocyanate and selenocyanate, their complexes with the divalent ions of electron configuration d^{10} , *viz.* Zn^{2+} , Cd^{2+} , and Hg^{2+} have been investigated.^{1,2} These ions show a large variation in their bonding properties, from the distinctly hard Zn^{2+} to the very soft Hg^{2+} . Results pertaining to the thiocyanate complexes of Zn^{2+} , Cd^{2+} , and Hg^{2+} and the selenocyanate complexes of Zn^{2+} and Cd^{2+} have already been reported.^{1,2} The free energy changes, ΔG_j° , have been computed from the stability constants while the enthalpy changes, ΔH_j° , have been measured with a titration calorimeter. Finally, the entropy changes, ΔS_j° , have been obtained from the relation

$$\Delta G_j^\circ = \Delta H_j^\circ - T \Delta S_j^\circ \quad (1)$$

The mercury(II) selenocyanate system could not be investigated in the same manner as the

corresponding zinc and cadmium systems, because of the rather strong acidic properties of Hg^{2+} .³ In solutions acid enough to suppress the hydrolysis of Hg^{2+} , the selenocyanate ion disintegrates rapidly. In order to ensure the stability of SeCN^- , the pH must in fact be $\gtrsim 5$.⁴

As the complex formation proceeds, however, the acidity of the mercury(II) species rapidly decreases so that the higher complexes $\text{Hg}(\text{SeCN})_3^-$ and $\text{Hg}(\text{SeCN})_4^{2-}$ seem to be stable in solution. This fact was utilized in the present investigation.

A stable mercury(II) selenocyanate solution was prepared by dissolving HgO in a selenocyanate solution strong enough to ensure the complete formation of the final complex $\text{Hg}(\text{SeCN})_4^{2-}$.^{5,6} The enthalpy change, $\Delta H_{\beta_4}^\circ$, for the reaction, $\text{Hg}^{2+} + 4\text{SeCN}^- \rightarrow \text{Hg}(\text{SeCN})_4^{2-}$, has been determined by measuring the heats of solution of HgO in selenocyanate and perchloric acid solutions. By combination of these enthalpy changes with the heat of neutralisation, $\Delta H_{\beta_4}^\circ$ can be computed.

The enthalpy changes, ΔH_j° , for the formation of mercury(II) thiocyanate complexes have previously been determined calorimetrically by the well-established titration technique.¹ In order to check the reliability of the method of dissolution used in this study, the value of $\Delta H_{\beta_4}^\circ$ has been redetermined by measuring the heat of solution of HgO in excess thiocyanate solution.

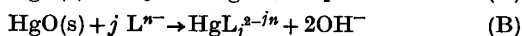
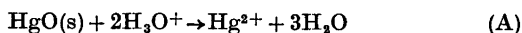
Another interesting sulfur donor, *viz.* the thiosulfate ion, $\text{S}_2\text{O}_3^{2-}$, also forms strong complexes with Hg^{2+} .^{7,8} Like the selenocyanate ion,

the thiosulfate ion disintegrates in acidic solution⁹ and an investigation of its mercury(II) complexes therefore poses the same difficulties. The stability constants for the formation of the second and third complexes have nevertheless been determined,^{7,8} but no determination of the enthalpy changes seems to have been reported so far. By measuring the heats of solution of HgO in acid as well as in thiosulfate solution, the enthalpy change for the formation of the highest complex formed, $\text{Hg}(\text{S}_2\text{O}_3)_3^{4-}$, has been obtained.

All measurements in this study have been performed at 25.00 °C in an aqueous medium of ionic strength $I = 1.00$ (0.30 M) with sodium perchlorate as supplementary electrolyte. The lower ionic strength was used for some measurements in the selenocyanate system.

CALCULATIONS

The enthalpy changes, ΔH_A and ΔH_B , for the following two reactions were experimentally determined

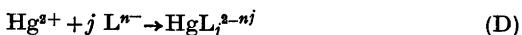


where HgL_j^{2-jn} denotes the saturated mercury(II) complex, which under the experimental conditions is formed quantitatively.

The enthalpy change ΔH_C of the reaction



in a perchlorate medium of $I = 1.00$ M has been found to be $-56.11 \text{ kJ mol}^{-1}$.¹⁰ The enthalpy change, ΔH_D , of the complex formation reaction



is

$$\Delta H_D = \Delta H_B - \Delta H_A + 2\Delta H_C \quad (2)$$

All uncertainty intervals given for ΔH in this paper are three standard deviations of the mean, $3[\sum \delta^2/n(n-1)]^{1/2}$.

EXPERIMENTAL

Chemicals. Red mercury(II) oxide in the form of a fine powder (Mallinckrodt Analytical Reagent) was used without further purification. Its purity was checked by means of an X-ray powder photograph. Sodium thiosulfate stock solutions were prepared from Merck reagent

grade crystals and redistilled water. In order to prevent decomposition of thiosulfate Na_2CO_3 (0.2 %) was added to the $\text{Na}_2\text{S}_2\text{O}_3$ solutions. Potassium selenocyanate solutions were prepared from the B.D.H. Analytical Reagent, which was used without further purification. Sodium thiocyanate and sodium perchlorate solutions were prepared and analyzed as before.¹

Calorimetric apparatus and procedure. The thermochemical measurements were carried out in a reaction solution calorimeter of the isothermal jacket type described by Sunner and Wadsö.¹¹ The calorimeter consists of an outer chromium plated brass can and a 90 cm³ inner reaction vessel made of glass. This reaction vessel contains a 2 000 Ω thermistor temperature sensor, a 20 Ω manganin wire heater and a combined stirrer-ampoule holder. The calorimeter in its jacket was completely immersed in a water thermostat maintained at 25.000 ± 0.001 °C. The Wheatstone bridge used for determining the change in resistance of the thermistor and the calibration unit were the same as used previously.¹²

In the main experiments HgO (0.10–0.50 g) was weighed into an ampoule. Standard LKB ampoules made of thin-walled Pyrex glass were used. After filling, the ampoules were sealed by closing the ampoule shaft with a tightly fitting silicon rubber stopper which then was covered with a thin layer of microwax. The sealed ampoule was put into the calorimeter where it was held by a four-pronged stirrer which could be lowered to break the ampoule on a sapphire tipped metal pin without interrupting the stirring. The reaction vessel filled with 80.0 ml of a solution was placed in the calorimeter and the temperature was brought to just under 25 °C. It was then sealed in its jacket and immersed in the 25.00 °C thermostat. By stirring the solution in the reaction vessel a smooth increase of its temperature was obtained. As the reactions were slow it was difficult to obtain a linear after-period, but an acceptable linearity could nevertheless be achieved if the ampoule breaking was initiated at such a temperature as to give an almost constant final temperature. However, the deviation of the mean temperature of the experiment from 25.00 °C was never larger than 0.02 °C. Electrical calibrations were made over the same temperature range as in the main experiment.

The temperature change obtained in a calibration was measured with an estimated precision corresponding to ± 0.03 J. In the main experiments the precision was generally somewhat lower due to the lengthy extrapolations of the temperature-time curve necessitated by the fairly slow dissolution reactions.

Testing of the calorimeter. To test the overall performance of the calorimeter, the enthalpy of solution of tris(hydroxymethyl)aminomethane, THAM, in 0.1 M HCl was measured. The result should be representative for rapid, moderately exothermic reactions.¹³ Varying amounts of

THAM (0.20–0.30 g) were dissolved in 80.0 cm³ 0.1000 M HCl. The mean value of $-\Delta H$ was (29.83 ± 0.09) kJ mol⁻¹ which is in good agreement with previously reported values. The 'best' value has been given as $-\Delta H = 29.75$ kJ mol⁻¹.¹⁴

MEASUREMENTS AND RESULTS

For the determination of the enthalpy change ΔH_A , (p. 983), the heats evolved on dissolution of varying amounts (0.25–0.40 g) of HgO in 1.00 M HClO₄ were measured. The amounts of HgO used were completely dissolved within about 20 min. The results are given in Table 1.

Mercury(II) thiocyanate. Varying amounts (0.28–0.36 g) of mercury(II) oxide were dissolved in 1.00 M NaSCN. The value of ΔH_B found is independent of the amount of HgO used, Table 2. At the prevailing [SCN⁻] all mercury(II) certainly exists as the complex Hg(SCN)₄²⁻.¹⁵ From eqn. (2), a value of the enthalpy change, $\Delta H_D = \Delta H_{\beta_4} = (-145.3 \pm 0.8)$ kJ mol⁻¹ is found for the formation of the fourth mercury(II)–thiocyanate complex. From the value of β_4 found by Ciavatta and Grimaldi¹⁵ for the same medium and temperature the value of $\Delta G^\circ_{\beta_4}$ entered in Table 4 has been calculated and finally, by combining $\Delta H^\circ_{\beta_4}$ and $\Delta G^\circ_{\beta_4}$, also the value of $\Delta S^\circ_{\beta_4}$.

Mercury(II) selenocyanate. Varying amounts of HgO were dissolved in 1.00 M KSeCN, Table 2. In all previous experiments a sodium ion medium has been used but in the present case the potassium ions were kept, as an exchange causes some disintegration of selenocyanate resulting in a very undesirable formation of cyanide, as discussed below. No significant difference in the enthalpy changes is to be expected between a potassium and a sodium ion medium.

Table 1. Heat of solution of HgO in 80.0 cm³ 1.00 M HClO₄.

mg of HgO	Q/J	$-\Delta H_A$ kJ mol ⁻¹
30.84	3.230	22.7
33.33	3.512	22.8
24.06	2.486	22.4
40.58	4.300	23.0
35.64	3.805	23.1
Mean value		22.8 ± 0.4

Table 2. Heat of solution of HgO in thiocyanate and selenocyanate solutions.

C_L/M	mg of HgO	Q/J	$-\Delta H_B$ kJ mol ⁻¹
SCN ⁻			
1.00	34.55	8.901	55.8
1.00	36.48	9.324	55.4
1.00	28.27	7.253	55.6
1.00	34.59	9.004	56.4
1.00	32.45	8.419	56.2
		Mean value	55.9 ± 0.5
SeCN ⁻			
1.00	27.59	13.175	103.4
1.00	46.78	22.468	104.0
1.00	38.58	18.339	103.0
1.00	57.23	26.904	101.8
1.00	32.83	15.754	103.9
		Mean value	103.2 ± 1.2
0.30	23.58	11.105	102.0
0.30	30.35	14.361	102.5
0.30	17.22	7.918	99.6
		Mean value	101.4 ± 2.7

Table 3. Heat of solution of HgO in sodium thiosulfate solutions.

C_L/mM	mg of HgO	Q/J	$-\Delta H_B$ kJ mol ⁻¹
335	28.88	9.524	71.4
335	34.89	11.469	71.2
335	31.79	10.386	70.8
335	32.28	10.540	70.7
170	17.67	5.788	71.0
170	13.07	4.420	73.2
170	24.31	8.212	73.2
85	17.64	5.707	70.1
85	24.15	7.808	70.0
85	18.14	6.114	73.0
		Mean value	71.5 ± 1.2

Selenocyanate solutions always contain impurities of cyanide ions. As the mercury(II)–cyanide system is much stronger than the corresponding selenocyanate system^{5,16} and as moreover the selenocyanate is used in large excess over mercury(II), even a very small amount of cyanide ions in the selenocyanate solution may give quite erroneous results. The cyanide will react with mercury(II) before the reaction between mercury(II) and selenocyanate starts.

Table 4. The stability constants used and the computed values of ΔG_j° , ΔH_j° , and ΔS_j° for the overall formation of $\text{Hg}(\text{SCN})_4^{2-}$, $\text{Hg}(\text{SeCN})_4^{2-}$, and $\text{Hg}(\text{S}_2\text{O}_3)_3^{4-}$.

Ligand <i>j</i>	SCN^- 4	SCN^- 4	SeCN^- 4	$\text{S}_2\text{O}_3^{2-}$ 3
β_j/M^{-j}	$(4.7 \pm 0.3) \times 10^{21a}$	$(4.7 \pm 0.3) \times 10^{21a}$	54×10^{28b}	1.8×10^{33c}
$\frac{-\Delta G_j^\circ}{\text{kJ mol}^{-1}}$	123.7 ± 0.2	123.7 ± 0.2	164.0	190.0
$\frac{-\Delta H_j^\circ}{\text{kJ mol}^{-1}}$	145.3 ± 0.8^d	141.6 ± 1.3^e	192.6 ± 1.5	160.9 ± 1.5
$\frac{\Delta S_j^\circ}{\text{J mol}^{-1}\text{K}^{-1}}$	-72 ± 4	-60 ± 5	-96 ± 5^f	98 ± 6^f

^a From Ref. 15. ^b From Ref. 5. ^c From Ref. 7. ^d This study. ^e From Ref. 1. ^f The error limits of ΔS_j° are calculated from the error limits of ΔH_j° only, as those of β_j (ΔG_j°) are not stated in Ref. 5 and Ref. 7. However, the error limits of ΔG_j° are generally small in comparison to those of ΔH_j° .

This reaction is considerably more exothermic than the formation of the selenocyanate complexes.^{5,16} By dissolving various amounts of HgO in a selenocyanate solution different values of the heats of solution, ΔH_B , should therefore be obtained if cyanide ions were present. Such a test has been performed. From a plot of ΔH_B versus the amount of HgO used the concentration of cyanide was found to be $\approx 0.2\%$ of that of selenocyanate. In order to eliminate this source of error, a small amount of mercury(II) (≈ 5 mM) was added to the 1.00 M selenocyanate solutions before they were used for the main experiments. In this way all free cyanide ions were removed by complex formation. The mercury(II) had to be added to the selenocyanate solutions just before use as mercury(II) selenocyanate, at too high concentrations, disintegrates on standing giving a black precipitate, probably of elemental selenium. In cases where large amounts of HgO were dissolved in selenocyanate the same precipitate was observed after the reaction also in the main experiments. As the temperature varied quite normally during the after periods, however, this slight precipitation is not likely to introduce any errors. The results are given in Table 2. No variation of ΔH_B with the amount of HgO is found which proves that no free cyanide ions were present in the selenocyanate solutions used. Toropova⁵ has studied the mercury(II)–selenocyanate system potentiometrically at 25 °C. Thus for the formation of the fourth mer-

cury(II)–selenocyanate complex she found $-\Delta G_{\beta_4}^\circ = 164.0$ and 164.9 kJ mol⁻¹ for $I = 0.8$ and 0.3 M, respectively. From the stability constants it is evident that in the present solutions all mercury(II) exists in the form of $\text{Hg}(\text{SeCN})_4^{2-}$. From eqn. (2) the enthalpy change for the formation of the fourth mercury(II) selenocyanate complex is found as $-\Delta H_{\beta_4}^\circ = (192.6 \pm 1.5)$ kJ mol⁻¹. Assuming $\Delta G_{\beta_4}^\circ$ has the same value at $I = 1.0$ M as at $I = 0.8$ M, the entropy change, $\Delta S_{\beta_4}^\circ$, has been obtained from eqn. (1), Table 4.

Some experiments were performed at lower selenocyanate concentration and ionic strength. Varying amounts of HgO were dissolved in a 0.300 M KSeCN solution, Table 2. As before, mercury(II) ($C_{\text{Hg}} = 1.5$ mM) was added to the selenocyanate solutions in order to remove free cyanide ions. In these experiments no precipitate of selenium was observed. Due to the low selenocyanate concentration it took a fairly long time (≈ 20 min) to dissolve the HgO, which detracts from the precision of the determination. The mean value of $-\Delta H_B = (101.4 \pm 2.7)$ kJ mol⁻¹ evidently agrees with that found at $I = 1.0$ M which shows that the slight disintegration taking place at the higher concentration is of no importance. Moreover the same mercury species, $\text{Hg}(\text{SeCN})_4^{2-}$, evidently predominates at both the selenocyanate concentrations used.

Mercury(II) thiosulfate. Varying amounts of HgO were dissolved in thiosulfate solutions of unit ionic strength. The measurements were

performed at three different thiosulfate concentrations, *viz.* 85, 170, and 335 mM, Table 3. At the lowest concentration used it took up to 30 min to dissolve the oxide. The stability constants of the mercury(II)–thiosulfate system have been determined polarographically at 25 °C at $I = 1.0$ M by Nyman and Salazar⁷ and at $I = 0.2$ M by Murayama *et al.*⁸ They agree that the third complex, $\text{Hg}(\text{S}_2\text{O}_3)_3^{4-}$, predominates at the concentrations used in the present measurements. Within the limits of error, the same value of ΔH_B is found for the three thiosulfate concentrations used, Table 3. This proves that within the range of concentrations used all mercury(II) exists in the same form, $\text{Hg}(\text{S}_2\text{O}_3)_3^{4-}$. As the third stepwise stability constant, K_3 , is much lower than the first two it is plausible that the third step is accompanied by a much smaller heat change than the first two. Thus even if some of the mercury(II) should exist in the form of the second complex, $\text{Hg}(\text{S}_2\text{O}_3)_2^{2-}$, it should not change the value of ΔH_B noticeably. The mean value of ΔH_B is (-71.5 ± 1.2) kJ mol⁻¹ and hence $\Delta H^\circ\beta_3 = (-160.9 \pm 1.5)$ kJ mol⁻¹ for the formation of the third mercury(II)–thiosulfate complex. The value of $\Delta G^\circ\beta_3$ was calculated from $\beta_3 = 1.8 \times 10^{33}$ M⁻³ found by Nyman and Salazar, and finally $\Delta S^\circ\beta_3$ according to eqn. (1). The results are given in Table 4.

DISCUSSION AND CONCLUSIONS

Shehukarev *et al.*¹⁷ have determined ΔH_A for the solution of yellow HgO in perchloric acid of different concentrations at 25 °C. For an acid concentration of 1.1 M they found $\Delta H_A = -22.80$ kJ mol⁻¹, in very good agreement with the present value $\Delta H_A = -22.8$ kJ mol⁻¹, for the solution of red HgO in 1.0 M HClO₄. This is expected as the heat of transformation between yellow and red HgO is small.¹⁸

For the mercury thiocyanate system the value of $-\Delta H^\circ\beta_4 = (145.3 \pm 0.8)$ kJ mol⁻¹ found here agrees satisfactorily with the value $-\Delta H^\circ\beta_4 = (141.6 \pm 1.3)$ kJ mol⁻¹ obtained by means of titration calorimetry in a previous study.¹ This shows that the method of determining enthalpy changes used in this study works satisfactorily.

For the mercury(II)–selenocyanate system Toropova⁵ has determined $\Delta H^\circ\beta_4$ from the

variation of β_4 with T in the temperature interval $15 < T < 30$ °C. Within the error limits the result, $-\Delta H^\circ\beta_4 = (195 \pm 5)$ kJ mol⁻¹, is in accord with that found in this study, Table 4.

Thiocyanate and selenocyanate are ambidentate ligands, coordinating *via* S or Se, respectively, or *via* N. Coordination *via* S and Se is preferred by soft acceptors, while hard ones prefer the harder N. Selenium donors are moreover found to be softer than analogous sulfur donors¹⁹ and should therefore give stronger complexes with soft acceptors. If an acceptor is coordinated *via* S and Se, the selenocyanate complexes should therefore be stronger than the thiocyanate ones and moreover formed in considerably more exothermic reactions.²⁰ The entropy terms should be of minor importance and of the same order of magnitude for the two ligands.² If, on the other hand, the N atoms are coordinated, the strength of the thiocyanate and selenocyanate complexes should be much the same. In this case the bonds formed will be less covalent and consequently the reactions much less exothermic than in the case of S or Se coordination. The bonds formed will be little influenced by an exchange of S for Se and much the same value of ΔH°_j should therefore be expected for thiocyanate and selenocyanate complexes. Theoretical calculations²¹ further indicate that coordination *via* N would bring about a larger decrease of charge on S than on Se, resulting in a larger gain of entropy in the former case. Coordination *via* N would thus entail a more positive or less negative entropy change for thiocyanate than for selenocyanate complexes.

For mercury(II) the selenocyanate complexes are considerably stronger than the thiocyanate complexes due to a much more negative value of $\Delta H^\circ\beta_4$, Table 4. For both systems the reactions are highly exothermic. The entropy terms are of the same magnitude and counteracting the complex formation. The results thus confirm the views expressed previously²² that mercury(II) is coordinated to the selenocyanate and thiocyanate ions *via* the soft Se and S atoms, respectively.

In the case of Cd²⁺, the selenocyanate complexes are again stronger than the thiocyanate complexes and moreover formed in more exothermic reactions while the entropy terms are of the same magnitude for the two systems.²

This indicates that also the borderline acceptor Cd^{2+} , at least partly, coordinates the ligands *via* the softer S and Se atoms, respectively. The covalent bonds formed are obviously much weaker than those formed by Hg^{2+} , however.

The thiocyanate and selenocyanate complexes of Zn^{2+} are quite weak, the latter being the weaker of the two.² The values of ΔH°_1 are slightly exothermic and of the same order of magnitude for both systems while the value of ΔS°_1 is less negative for thiocyanate. This strongly indicates coordination *via* N for both systems.

Following the general rule, the coordination of both thiocyanate and selenocyanate thus becomes more exothermic the softer the acceptor. Especially the difference between the very soft Hg^{2+} and the borderline acceptor Cd^{2+} is, as expected, very large. However, the difference between Cd^{2+} and the hard acceptor Zn^{2+} is also quite significant.

During the course of formation of zinc and cadmium selenocyanate complexes changes of coordination figure probably occur,² involving a switch from the octahedral aquo ions of Zn^{2+} and Cd^{2+} to the tetrahedral coordination represented by the final complexes $\text{Zn}(\text{SeCN})_4^{2-}$ and $\text{Cd}(\text{SeCN})_4^{2-}$, respectively. The switch causes an irregular variation of ΔS°_j between the consecutive steps and the trend is moreover quite different for the thiocyanate and the selenocyanate systems. As may be expected, however, the values of ΔS°_j are small and negative and generally more negative the softer the acceptor.²⁰

For the mercury(II)–thiosulfate system the value of $\Delta H^\circ_{\beta_3}$ is, as expected for a sulfur donor, strongly exothermic, Table 4. The entropy term, $\Delta S^\circ_{\beta_3} = 98 \text{ kJ mol}^{-1} \text{ K}^{-1}$, is also contributing to the strong complex formation. For the thiocyanate and selenocyanate systems of mercury(II) the entropy terms, $\Delta S^\circ_{\beta_4}$, are negative, Table 4. The large differences between the entropy terms of the thiosulfate system on the one hand and the thiocyanate and selenocyanate systems on the other are explained by the difference in charge of the ligands. The divalent thiosulfate ion is certainly more structure-ordering than the monovalent thiocyanate and selenocyanate ions. Thus coordination of $\text{S}_2\text{O}_3^{2-}$ causes a more extensive structural breakdown resulting in the liberation of more water and

consequently in a more positive value of the entropy term.

Schwarzenbach and Schellenberg²⁴ have determined the thermodynamic parameters for the reaction $\text{CH}_3\text{Hg}^+ + \text{S}_2\text{O}_3^{2-} \rightarrow \text{CH}_3\text{HgS}_2\text{O}_3^-$ at 20 °C and $I = 0.1 \text{ M}$. They found $-\Delta H^\circ_1 = 61 \text{ kJ mol}^{-1}$ and $\Delta S^\circ_1 = 41 \text{ J mol}^{-1} \text{ K}^{-1}$. These values are quite in line with those of $\Delta H^\circ_{\beta_3}$ and $\Delta S^\circ_{\beta_3}$ found for the mercury(II)–thiosulfate system.

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